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Title of Invention

Electric conduction paste for thick films

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Specification

1. The name of invention

Electric conduction paste for thick films

2. Claim

Electric conduction paste for thick films made by coking precious-metals powder, such as Ag, Pd, Au, and Pt, with 49-91 % of the weight, glass frit with 6-20 % of the weight, and the powder consists of one or more metals from Zn, Al, and Sn with 3-31 % of the weight using binder.

3. Detailed Explanation of Invention

[Field of the Invention]

This invention relates to the electric conduction paste used for manufacturing a mixed integrated circuit etc. by thick film methods, such as the so-called screen-printing method.

[Prior Art]

In general, when circuit equipments, such as a mixed integrated circuit, are manufactured by the thick film method, a method that prints electric conduction paste according to a predetermined circuit pattern by the screen-printing method with the ceramic board as a base which has a

penetration hole, as well as fills up the above-mentioned penetration hole with this paste and bake them on is adopted.

To avoid the increase of resistance due to oxidization of a metal ingredient when calcining electric conduction paste in air, electric conduction paste which chiefly consists of precious metals, such as Ag, Au, and Pt, is used, but it is expensive.

Thus, the method of calcining the electric conduction paste which consists of base metals, such as nickel, as the main ingredients in inert gas, such as N<sub>2</sub> gas, is put in practical use for lower cost.

However, the resistance paste which has RuO<sub>2</sub> as the main ingredient, used for constituting a resistance film on the above-mentioned board, is needed to calcine in air.

For this reason, when constituting resistance film, the method was taken in which first calcines the electric conduction paste which made the base metal the main ingredient, then the base metal conductor exposed outside is plated with the precious metals to prevent oxidization, then prints the electric conduction paste and the above-mentioned resistance paste which make the precious metals the main ingredient on this.

[The problem which invention intends to solve]

However, for the procedure of oxidization prevention by precious metal plating, first, nickel plating is giving only to base metal conductor exposed to the surface of a ceramic board, and then it is preceded by precious metal plating.

Therefore, a comparatively complicated process is needed and a result which reduces sharply the cost reduction effect acquired when this uses base metal paste is brought.

This invention is to solve the above-mentioned conventional problem. Noting that adding a little Zn, Al, or Sn to electric conduction paste consisting of precious metal and glass frit, and pasting and calcining it on the surface of base metal conductor prevents this base metal conductor from oxidizing, printing directly electric conduction paste and calcining it in air was enabled without special oxidization prevention processing, such as precious metal plating.

[Means for solving problem]

As for this invention, the electric conduction paste for thick films consists of the precious metal powder, such as Ag, Pd, Au, and Pt, with 49-91 % of the weight, glass frit with 6-20 % of the weight, and one or more powders selected from Zn, aluminum, and Sn with 3-31 % of the weight.

Generally borosilicate glass, such as CaO-BaO-SiO<sub>2</sub> system glass, is used for glass frit.

[Action]

When using the electric conduction paste of this invention, precious-metals plating is not carried out to the surface of base metal conductor calcined in inert gas, but this paste is directly printed in layers on this, and this is calcined in air.

Then, a continuity state required for electric connection of a circuit is acquired at the point of contact with conductor which was obtained by calcining base metal conductor with the above-mentioned electric conduction paste.

This is considered to be based on a reason like the next.

When the above-mentioned electric conduction paste is calcined in air, the metals present near the boundary of the base metal conductor, such as Zn, Al, Sn, take the oxygen from the aforementioned base metal conductor and are oxidized, then taken in and disperse into the sintered glass component.

For this reason, near the surface of base metal conductor, so to speak, metal ingredients, such as nickel in it, will be in a reduced state, it will not be oxidized but reacts with the precious-metals ingredient, such as Ag, Pd, Au, and Pt, etc., in the above-mentioned electric conduction paste, and an electric continuity state is formed.

In addition, the reason to limit the composition ratio of electric conduction paste as mentioned above is as following.

(1) If there is much metal powder, such as Zn, aluminum, and Sn, the quantity of the oxide produced when electric conduction paste is calcined in air will increase and the oxide disperses so much in a glass ingredient. As a result, there is a tendency for the adhesion intensity of conductor to drop.

Moreover, the above-mentioned oxide which exists in precious-metals powder boundary, without dispersing in glass raises the resistance of conductor.

From this point, these practically need to be 31% or less of the weight.

Moreover, a minimum of 3% of the weight of a composition ratio is required to do the above-mentioned action.

(2) Too few glass ingredients lowers adhesion intensity between conductor and too much glass ingredient raises the contact resistance between conductor because the sintered glass ingredient covers the junction side of between conductors.

6-20% of the weight of a composition ratio is required from this point.

#### [Effect of the Invention]

The effect of this Invention is explained below.

The electric conduction paste which has the composition, which adds 6g of ethyl cellulose 33g of  $\alpha$ -terpineol, as a binder, to 63g of Ag powder, 12g of Pd powder, 6g of Zn powder, and 19g of CaO-BaO-SiO<sub>2</sub> system glass frit, mixed by three-step roll mil, shown by the sample number 55 of an attached table was made.

Furthermore, in addition to this, by the same method, the electric conduction paste which has the composition shown by the sample number 3-5 of an attached table, 7-9, 13-17, 21 and 22, 24-26, 29-33, 36-39, 43-45, 49, 50 and 52, 54-61, 64-71, 73-77, and 79-85 was made, respectively.

[Working Examples]

Next, the electric conduction paste obtained in the above-mentioned case of the invention was used by method like the next, and examined.

While screen-printing the electric conduction paste which makes nickel the main ingredients on a non-sintered porcelain sheet with a thickness of 200 micrometers which has multiple penetration holes according to a predetermined circuit pattern, the hole was filled up with the above-mentioned electric conduction paste.

Subsequently, after heating this non-sintered porcelain sheet for 10 minutes at the temperature of 125 DEGC and drying, in a predetermined order, four-sheet laminating was carried out and it was stuck by pressure.

Subsequently, after heat-treating this at the temperature of 900 DEGC and removing the binder ingredient under a porcelain sheet and electric conduction paste, the multilayer wiring board as shown was made by placing it under the temperature of 1200 DEGC in N<sub>2</sub> gas atmosphere containing 2% of H<sub>2</sub> for 2 hours.

At this point, the intensity of resistance between conductors 2, 2 which were mutually connected inside of substrates 1, 1 was measured at between the conductor surfaces 2a and 2b which are exposed on the surface of the top substrate.

The electric conduction paste obtained in the above-mentioned case of the invention was used next, this paste was screen-printed so that it covers conductor surface exposed to the surface of the outmost substrate 1, and the temperature of 850 DEGC was given to calcined this in air for 10 minutes, and conductor 3, 3 was formed.

In addition, drawer electrode section 5 of 1mm angle was formed at the end of a substrate at this time.

Subsequently, the resistance paste which makes RuO<sub>2</sub> the main ingredients was printed on conductor 3 and 3 which were newly prepared, in air, the temperature of 850 DEGC was given for 10 minutes, this was calcined, and the resistance film 4 was produced on the substrate 1.

And the increase in the resistance intensity was not seen when the resistance intensity of the above-mentioned conductor 2 and 2 was measured on the surface 3a and 3b of this conductor 3 and 3 before and after the creation of the afore-mentioned conductor 3 and 3 and the resistance film 4, and ratios to the above-mentioned resistance intensity taken at the conductor surfaces 2a and 2b were taken, but both were 1.00, even after calcining in oxidized atmosphere.

This is shown as "O" in the column of the continuity characteristic on an attached table.

Moreover, each tension intensity in case this electrode section 5 exfoliates from the substrate 1 surface was more than 1.0kg/mm<sup>2</sup> as it was shown in an attached table, when the lead 6 of 0.5φ was attached to above-mentioned electrode section 5 soldering 7, and this lead 6 was pulled perpendicularly and examined to the surface of a substrate 1.

[The example of comparison]

To the above-mentioned case of the invention, for comparison, as shown in each column of the sample numbers 1, 2, and 6, 10-12, 18-20, 23, 27, 28, 34 and 35, 40-42, 46-48, and 51, 53, 62, 53, 72 and 78 of an attached table, the sample, which the composition ratio does not fill the above-mentioned requirements although the same ingredient as the electric conduction paste by this invention is included, were made in the same way as the above-mentioned case of the invention, and used and examined in the same conditions as the as the above-mentioned example of use, and the example of an examination.

Consequently, the ratio of the resistance measured between conductor surface3a and 3b, respectively and the resistance measured between conductor surface2a and 2b exceeded 1.00 before and after the production of conductor 3 and 3 and the resistance film 4, or ("x" showed that to which the ratio of this resistance exceeds 1.00 to the column of the continuity characteristic of an attached table) tension intensity was less than 1.0kg/mm<sup>2</sup> as shown in each column of an attached table.

[Effect of invention]

As explained above, with this invention, continuity characteristic required to constitute an electric circuit without oxidizing conductor surface can be obtained only by printing electric conduction paste directly onto the above-mentioned surface of base metal conductor to cover it and calcining it in air, without special oxidization prevention processing, such as precious metal plating on the surface of base metal conductor.

For this reason, reduce in man-hour when manufacturing circuit equipments, such as a mixed integrated circuit, can be aimed at.

#### 4. Brief Explanation of the Drawings

The drawing is outline drawing of longitudinal section with expanded size of thickness direction of the multilayer interconnection porcelain baseplate, in which the example of use of the electric conduction paste of this invention is shown.

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Attached table

\* The sample produced as an example of comparison is shown.

Sample number	Constitution ratio (weight %)								Continuity characteristics	Intensity of tension (kg/mm <sup>2</sup> )
	Ag	Pd	Au	Pt	Glass	Zn	Al	Sn		
1	92				5	3			O	0.8
2	91				6.5	2.5			X	1.2
3	91				6	3			O	1.2
4	85				10	5			O	1.8
5	70				20	10			O	2.0
*6	69				21	10			X	2.0
7	60				19	21			O	1.5
8	55				15	30			O	1.2
9	49				20	31			O	1.0
*10	48				20	32			O	0.8
*11	92				5			3	O	0.7
*12	91				6.2			2.8	X	1.3
13	91				6			3	O	1.2
14	72				12			16	O	1.8
15	65				10			25	O	1.5
16	54				20			26	O	1.3
17	49				20			31	O	1.1
*18	48				20			32	O	0.9
*19	48				21			31	X	0.8
*20		91			6.2	2.8			X	1.1
21		91			6	3			O	1.2
22		79			13	8			O	1.5
*23		75			5	20			O	0.5
24		74			6	20			O	1.2
25		57			16	27			O	1.3
26		49			20	31			O	1.0
*27		48			21	31			X	0.8
*28		49			19	32			O	0.8
29		93			4.5		2.5		X	1.2
30		91			6		3		O	1.3
31		76			8		16		O	1.8
32		62			15		23		O	1.2
33		49			20		31		O	1.0
*34		48			20		32		O	0.9
*35			94		6				X	1.2
36			91		6			3	O	1.3
37			73		8			19	O	1.2
38			53		19			28	O	1.3
39			49		20			31	O	1.0
*40			48		21			31	X	0.9

\* The sample produced as an example of comparison is shown.

Sample number	Constitution ratio (weight %)								Continuity characteristics	Intensity of tension (kg/mm <sup>2</sup> )
	Ag	Pd	Au	Pt	Glass	Zn	Al	Sn		
*41			49		19			32	O	0.8
*42			92		5				O	0.8
43			91		6				O	1.2
44			64		13				O	1.5
45			49		20				O	1.1
*46			50		18				O	0.8
*47	68	12			20				X	2.0
*48	68	12			17.1	2.9			X	2.0
49	69	22			6	3			O	1.2
50	68	13			16	3			O	1.8
*51	68	8			21	3			X	2.0
52	68	9			20	3			O	2.0
*53	68	24			5	3			O	0.9
54	62	25			10	3			O	1.8
55	63	12			19	6			O	2.0
56	17	57			16	10			O	1.8
57	51	15			15	19			O	1.5
58	50	17			8	25			O	1.3
59	48	8			14	30			O	1.2
60	41	19			10	30			O	1.2
61	41	19			9	31			O	1.0
*62	8	40			20	32			O	0.9
*63	68	12			17.5			2.5	X	2.0
64	20	60			17			3	O	2.0
65	56	18			18			8	O	1.8
66	16	50			18			16	O	1.7
67	46	15			17			22	O	1.5
68	49	19			6			26	O	1.2
69	42	14			14			30	O	1.1
70	41	14			14			31	O	1.0
71	24	25			20			31	O	1.0
*72	67			13	17.4		2.6		X	2.0
73	66			25	6		3		O	1.2
74	58			15	13		14		O	1.5
75	15			46	9		30		O	1.1
76	46			15	8		31		O	1.0
77	4			45	20		31		O	1.1
*78	8			40	20		32		O	0.9
79	87	4			6	2	1		O	1.2
80	80	11			6	1	1	1	O	1.1

\* The sample produced as an example of comparison is shown.

Sample number	Constitution ratio (weight %)								Continuity characteristics	Intensity of tension (kg/mm <sup>2</sup> )
	Ag	Pd	Au	Pt	Glass	Zn	Al	Sn		
81	69	12			10		6	3	O	1.8
82	63	11			15	5	2	4	O	1.5
83	49	7			14	10	10	10	O	1.2
84	19	61			12	1	4	3	O	1.9
85	24	25			20	20	2	9	O	1.0

